SEMI-CLASSICAL THEORY OF ELECTRONIC EXCITATION RATES

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INTRODUCTION

At high temperatures, the properties of a gas are influenced by vibrational excitation, dissociation, electronic excitation, and ionization; all sinks of energy which absorb some of the kinetic energy of molecular motion and change the thermodynamic and transport properties of the gas rather strongly. Moreover, the different modes of energy may not relax to equilibrium in the time scale of concern, for example the dwell time of the flow about a hypersonic vehicle. Usually, however, the collisions will establish a Boltzmann like distribution of states within each energy mode very quickly; only a few collisions are required to randomize the kinetic energy states in a most probable distribution, and to a first approximation the same is true of the molecular vibrational states if one neglects the distortion of the distribution that occurs due to anharmonicity in the upper vibrational levels. Although the exchange of kinetic energy is minimal in collisions between free electrons and heavy particles, the electron-electron collisions quickly establish a Boltzmann distribution of electron kinetic energy states. This state of pseudo steady nonequilibrium is described by a gas with three different temperatures; T, T_e, and T_v. These temperatures describe the Boltzmann distributions of heavy particle kinetic energy, of electron kinetic energy, and of vibrational states respectively.

Experimentally, the transfer of energy between diatomic vibrational states and free electron kinetic energy is known to be very rapid. For example, this fact is used to establish vibrational population inversions in the CO Electric Discharge Supersonic Laser[1]. Moreover, the calculation of diatomic vibrational excitation by electron collision has been calculated using first principles[2,3], and the relaxation of free electron-molecular vibration states towards equilibrium with one another is orders of magnitude faster than the relaxation of vibrational states by heavy particle collision[4]. Thus a reasonably good approximation for high temperature gases, at least in the time scale of concern in hypersonic flow problems, obtains when T_e and T_v are equalized[5].

The relaxation of excited electronic states of atoms and molecules toward equilibrium is not as well understood. The assumption is often used that excited electronic energy, like

vibrational energy, is in equilibrium with the free electron kinetic energy. Park[6] published some estimates of rate coefficients for electron bombardment excitation of N and O atoms, based on the work of Lotz[7], which indicate equilibration between free electron energy and excited electronic energy of the atoms is indeed rapid, comparable with rate coefficients for excitation of vibrational states by electron collision. Thus the approximation that excited electronic states are described by T_e is no doubt a reasonably good one.

However, once equilibration with electron collisions has been achieved, these collisions no longer change the distribution; additional energy to the vibrational and excited electronic modes feeds in from collision with heavy particles. A portion of this energy is in turn transmitted to free electron kinetic energy[4], and in fact the electron-vibration and electron-electronic state energy transfers are no doubt the principal mechanisms by which electron kinetic energy is eventually brought into full equilibrium with the heavy particle kinetic energy of the gas. The direct energy exchanges that occur in electron-heavy particle collisions are negligible in comparison.

In the case of vibrational excitation there exist some good experiments backed by reliable theories which provide quantitative vibrational relaxation rates[8-12], which can be used to predict the relaxation of hypersonic flow to full equilibrium at moderately high temperature. However, the rates for electronic excitation are needed to complete the picture at very high temperature. As suggested above, the equilibration between free electron kinetic energy and the excited electronic states of heavy particles is probably rapid. But the rate of electronic excitation by heavy particle collisions is required for prediction of electronic energy in the temperature range around 5000°K where normally few free electrons exist. When the free electrons do appear, the heavy particle excitation of electronic states is a channel that competes with vibrational excitation as a mechanism for equilibration of electron kinetic energy, and at higher temperatures where the molecules disappear the heavy particle excitation of electronic energy is probably the principal mechanism for this equilibration. Accordingly, the purpose of this paper is to develop a semi-classical theory of electron state excitation of atoms and molecules caused by collisions with heavy particles, and to compare the relaxation rates obtained in this process with the relaxation achieved by free electron collisions.

ELECTRONIC STATE RELAXATION BY ELECTRON COLLISION

Let the free electron kinetic temperature be T_e and the excited electronic state distribution be described by the temperature T^*. Assume that collisions between gas particles in excited states transfer electronic energy so readily that the

distribution becomes Boltzmann like quickly and that the relaxation of this process can be treated as instantaneous on the time scale of concern. Also assume that free electron collisions are the only effective means of introducing additional excited electronic state energy. Then the rate of change in electronic energy E^* is

$$\frac{dE^*}{dt} = n_e n \sum_{j=1}^{j_m} \sum_{i=o}^{j-1} (e_j - e_i)\left(\frac{n_i}{n} k_{ij} - \frac{n_j}{n} k_{ji}\right) \qquad (1)$$

where n_e is the number density of free electrons, n_i is the number density of atoms in state i with electronic energy e_i, n is the total number density of atoms, and k_{ij} is the rate coefficient for excitation from state i to j by free electron collision. Eq.(1) accounts for all upward and downward transitions in electronic state over all levels up to some maximum level j_{max}.

The number densities n_i are given by the temperature T^*

$$\frac{n_i}{n} = \frac{g_i\, e^{-e_i/kT^*}}{Q(T^*)} \qquad (2)$$

where g_i is the degeneracy of the i^{th} state and $Q(T^*)$ is the electronic state partition function of the atom

$$Q(T^*) = \sum_{j=o}^{j_{max}} g_i\, e^{-e_i/kT^*} \qquad (3)$$

By detailed balancing at equilibrium with the electron temperature T_e, the ratio of the rate coefficients is

$$\frac{k_{ji}}{k_{ij}} = \frac{g_i}{g_j}\, e^{-(e_i - e_j)/kT_e} \qquad (4)$$

Thus Eq.(1) can be expressed

$$\frac{dE^*}{dt} = n_e n \sum_{j=1}^{j_{max}} \sum_{i=0}^{j-1} (e_j - e_i)\left(\frac{n_i}{n}\right)_{T^*} k_{ij} \left(1 - \left(\frac{n_j}{n_i}\right)_{T^*}\left(\frac{n_i}{n_j}\right)_{T_e}\right) \qquad (5)$$

The deviation of electronic excitation energy per atom from its equilibrium value at the temperature T_e is

$$\Delta E^* = E^*(T_e) - E^*(T^*) = n \sum_i e_i \left(\left(\frac{n_i}{n} \right)_{T_e} - \left(\frac{n_i}{n} \right)_{T^*} \right) \qquad (6)$$

The product of electron density n_e and the relaxation time τ for the process is n_e times Eq.(6) divided by Eq.(5)

$$n_e \tau = \frac{n_e \Delta E^*}{(dE^*/dt)} \qquad (7)$$

Park[6] approximates the calculated values for the rate coefficients k_{ij} with the empirical form

$$k_{ij} = C_{ij} \left(\frac{T_e}{10000} \right)^{m_{ij}} e^{-(e_j - e_i)/kT_e} \qquad (8)$$

The values of the coefficients C_{ij} and m_{ij} given in Table 2.1 of Park's book[6] were used to calculate the $n_e\tau$ products given by Eq.(7). The results for N atom relaxation are shown in Fig.(1) and for O atom relaxation in Fig.(2). Note that the relaxation is insensitive to the initial electronic temperature T^*. The relaxation rates are expected to decrease monotonicly as temperature increases. For e-N collisions this expectation is satisfied except for very low values of temperature, where the rate coefficients given by Eq.(8) are no doubt unreliable. However for the case of e-O collisions, the results look very strange indeed. The relaxation rate increases at temperatures above 15000 degK and plateaus unrealistically at still higher temperature. Probably this is an artifact which results because so many of the excitation rate coefficients are essentially zero in Park's table for e-O collisions, which seems physically unlikely. Some modification of the constants C_{ij} not specified in Ref.(6) has been applied by Park in Ref.(13), but that is unlikely to compensate for the missing rate coefficients in the relaxation rate calculation. However that may be, the density relaxation time products are very short, the order of 10^{-17} to 10^{-18} mol sec/cc. This is even smaller than the density relaxation times for electron collision production of vibrational states[4] (where $n_e\tau$ is the order of 10^{-15} to 10^{-16} mol sec/cc), so rapid equilibration of excited electronic states and free electron kinetic energy can be anticipated. The principal concern here is how these electron collision rates compare with rates for electronic state excitation by heavy particle collisions.

ELECTRONIC STATE EXCITATION BY HEAVY PARTICLE COLLISION

The atoms or molecules in high energy collision will be assumed to experience a simple exponential repulsion potential

$$U = A\, e^{-R/L} \tag{9}$$

where A is a constant which establishes the size of the collision potential and L is a scale factor which determines the steepness of the potential as the distance R between the collision partners changes. Since the major contributions to the transition probability will occur where the potential is the steepest, long range attractive parts of the potential can be accounted for by increasing the collision energy of the pair by the depth of the attractive well and adjusting A and L to duplicate the steepest part of the potential, which is in effect traversed with the velocity of this increased collision energy. The long range attractive forces between molecules will be rather negligible at high temperatures in any case. However, for the atomic collisions a deep attractive well occurs when the electron spins of the outer electrons of the colliding atoms happen to pair; then the higher effective collision energies will need to be taken into account.

For the potential of Eq.(9), the solution for the intermolecular distance as a function of time is analytic in the case of head on collision[11].

$$\frac{U}{E} = \exp\left(-\frac{R-R_o}{L}\right) = sech^2\frac{ut}{2L} \tag{10.1}$$

$$\frac{R}{R_o} = 1 - \frac{2L}{R_o}\ln sech\left(\frac{ut}{2L}\right) \tag{10.2}$$

where u is the collision velocity in center of mass coordinates, E is the collision energy ($\mu u^2/2$), and R_o is the distance of closest approach

$$R_o = L\ln(A/E) \tag{11}$$

If one of the collision partners makes a transition from state a to state b during the collision, the excited electron produces a dipole which creates an electric field V at the position of the other particle

$$V = \frac{e\, r\cos\theta}{R^3} \tag{12}$$

where r is the displacement of the electron charge e from its nuclear center and θ is the polar angle the vector r makes with the

intermolecular distance vector R as shown on Figure 3. A small perturbation energy ($-\alpha V^2$) occurs between the particles, due to the dipole induced in the inert collision partner (that is, the partner not making a transition), where α is the polarizability of that partner. This ripple perturbation added to the interaction of Eq.(9) gives the total interaction for collision when transition occurs.

$$U = A\, e^{-R/L} - \alpha V^2 \tag{9.1}$$

The small perturbation transition probability for promotion of state a to b is

$$P_{ab} = \frac{1}{\hbar^2} \left(\int_{-\infty}^{\infty} \langle \varphi_b^* | U | \varphi_a \rangle\, e^{i\omega_{ab}t}\, dt \right)^2 \tag{13}$$

where φ_a and φ_b are the spatially dependent parts of the wave functions for the states a and b respectively. The time dependent parts of the total wave function provide the circular frequency for the transition

$$\omega_{ab} = (E_b - E_a)/\hbar \tag{14}$$

The quantum average of the first term in Eq.(9.1) vanishes due to the orthogonality of the wave functions, and the resulting transition probability can be expressed as a product of several dimensionless factors

$$P_{ab} = \left((\alpha/a_o^3)\, (e^2/a_o \hbar\omega)\, (a_o/R_o)^6\, H_{ab}\, F_{ab} \right)^2 \tag{13.1}$$

The dimensionless transition matrix element H_{ab} is

$$H_{ab} = \langle \varphi_b^* \,|\, (r/a_o)^2 \cos^2\theta \,|\, \varphi_a \rangle \tag{13.2}$$

and the dimensionless Fourier transform is

$$F_{ab} = \omega_{ab} \int_{-\infty}^{\infty} \frac{e^{i\omega_{ab}t}\, dt}{(R/R_o)^6} \tag{13.3}$$

POLARIZABILITY OF ATOMS AND MOLECULES

The polarizability of multielectron atoms and molecules needed in Eq.(13.1) is a function of frequency

$$\alpha = \frac{e^2}{m} \sum_i \frac{(\omega_i^2 - \omega_{ab}^2)\ f_i}{(\omega_i^2 - \omega_{ab}^2)^2 + 4\gamma^2\omega_{ab}^2} \qquad (15)$$

where the sum extends over all optical transitions of the inert collision partner, f_i is the oscillator strength of transition i, ω_i is the radian frequency of transition i, and γ is the damping coefficient

$$\gamma = \frac{\omega_{ab}^2\ e^2}{3mc^3} \qquad (15.1)$$

The oscillator strengths needed in Eq.(15) are tabulated for atoms by Weise, Smith, and Glennon[14], for example.

TRANSITION MATRIX ELEMENTS

Evaluation of the transition matrix elements of Eq.(13.2) requires knowledge of the wave functions φ_a and φ_b. Although these functions are not known precisely for atoms in general, the upper excited states at least are nearly hydrogen like, in which case the Slater type screened wave functions are a fair approximation. For the state of quantum number n

$$\varphi_n = R_{nlm}(Zr/n)\ Y_{lm}(\theta,\phi) \qquad (16)$$

where R_{nlm} is the usual hydrogenic radial wave function, Y_{lm} is the spherical harmonic angular function, and the effective screened charge Z is related to the observed energy E_n of the n^{th} quantum state

$$E_n = -\frac{Z^2}{n^2}\left(\frac{e^2}{2a_o}\right) \qquad (17)$$

Where the ground state is involved in the transition a somewhat better approximation may be required for the ground state wave function, such as the partial quantum number functions of Bates and Damgaard[15]. Although transition matrix elements determined with these approximate wave functions will not be exact, the correction factor should be the order of unity so the results will at least provide reasonable estimates of the magnitude of the transition probabilities and exhibit correct functional relations.

FOURIER TRANSFORMS

The Fourier transform given by Eq.(13.3) and Eq.(10.2) is

$$F = \omega \int_{-\infty}^{\infty} \frac{e^{i\omega t}\, dt}{\left(1-\frac{2L}{R_o} \ln sech\frac{ut}{2L}\right)^6} \qquad (18)$$

The subscripts a and b for the specific transition in question are omitted for economy in notation.

Transform the variables to

$$z = \frac{ut}{2L} \quad , \quad \beta = \frac{2\omega L}{u} \quad , \quad a = \frac{R_o}{2L} \qquad (18.1)$$

Then the dimensionless Fourier transform becomes

$$F = \beta \int_{-\infty}^{\infty} \frac{e^{i\beta z}\, dz}{(1-\frac{1}{a} \ln sech\ z)^6} \qquad (19)$$

The denominator of the integrand in Eq.(19) has sixfold roots at $\pm z_o$, where

$$z_o = i \arccos(e^{-a}) \qquad (19.1)$$

The integral of Eq.(19) is obtained by integrating around a half circle in the complex plane, along the real axis from $-\infty$ to $+\infty$ and then back along the half circle at infinity in the upper plane; this encloses the pole at $+z_o$. Then the integral along the real axis is just $2\pi i$ times the residue at $+z_o$.

$$\beta \int_{-\infty}^{\infty} \frac{e^{i\beta z}\, dz}{(1-\frac{1}{a} \ln sech\ z)^6} = 2\pi\beta i\ Res(z_o) \qquad (20)$$

The residue is obtained by multiplying the integrand with $(z-z_o)^6$, taking the 5^{th} derivative with respect to z, and then evaluating that derivative at z_o. This is a somewhat lengthy but straightforward process. The result is an analytic function of collision energy which can then be integrated over a Maxwell Boltzmann distribution of collision energies by numerical quadrature.

Define the functions G(z) and g(z)

$$G(z) = \frac{(z-z_o)^6\, e^{i\beta z}}{(1-\frac{1}{a}\ln sech\, z)^6} = \frac{e^{i\beta z}}{g^6(z)} \tag{21}$$

Then the derivatives of G are

$$\frac{dG}{dz} = \left(\frac{i\beta}{g^6} - \frac{6}{g^7}\frac{dg}{dz}\right)e^{i\beta z} \tag{21.1}$$

$$\frac{d^2G}{dz^2} = \left(-\frac{\beta^2}{g^6} - \frac{2\cdot 6\, i\beta}{g^7}\frac{dg}{dz} - \frac{6}{g^7}\frac{d^2g}{dz^2} + \frac{6\cdot 7}{g^8}\left(\frac{dg}{dz}\right)^2\right)e^{i\beta z} \tag{21.2}$$

$$\begin{aligned}\frac{d^3G}{dz^3} = &\left[-\frac{i\beta^3}{g^6} + \frac{6}{g^7}\left(3\beta^2\frac{dg}{dz} - 3i\beta\frac{d^2g}{dz^2} - \frac{d^3g}{dz^3}\right)\right.\\ &\left. + \frac{6\cdot 7}{g^8}\left(3i\beta\left(\frac{dg}{dz}\right)^2 + 3\frac{dg}{dz}\frac{d^2g}{dz^2}\right) - \frac{6\cdot 7\cdot 8}{g^9}\left(\frac{dg}{dz}\right)^3\right]e^{i\beta z}\end{aligned} \tag{21.3}$$

$$\begin{aligned}\frac{d^4G}{dz^4} = &\left[\frac{\beta^4}{g^6} + \frac{6}{g^7}\left(4i\beta^3\frac{dg}{dz} + 6\beta^2\frac{d^2g}{dz^2} - 4i\beta\frac{d^3g}{dz^3} - \frac{d^4g}{dz^4}\right)\right.\\ &- \frac{6\cdot 7}{g^8}\left(6\beta^2\left(\frac{dg}{dz}\right)^2 - 12i\beta\frac{dg}{dz}\frac{d^2g}{dz^2} - 4\frac{dg}{dz}\frac{d^3g}{dz^3} - 3\left(\frac{d^2g}{dz^2}\right)^2\right)\\ &\left. - \frac{6\cdot 7\cdot 8}{g^9}\left(4i\beta\left(\frac{dg}{dz}\right)^3 + 6\left(\frac{dg}{dz}\right)^2\frac{d^2g}{dz^2}\right) + \frac{6\cdot 7\cdot 8\cdot 9}{g^{10}}\left(\frac{dg}{dz}\right)^4\right]e^{i\beta z}\end{aligned} \tag{21.4}$$

$$\begin{aligned}\frac{d^5G}{dz^5} = &\left[\frac{i\beta^5}{g^6} - \frac{6}{g^7}\left(5\beta^4\frac{dg}{dz} - 10i\beta^3\frac{d^2g}{dz^2} - 10\beta^2\frac{d^3g}{dz^3} + 5i\beta\frac{d^4g}{dz^4} + \frac{d^5g}{dz^5}\right)\right.\\ &- \frac{6\cdot 7}{g^8}\left(10i\beta^3\left(\frac{dg}{dz}\right)^2 + 30\beta^2\frac{dg}{dz}\frac{d^2g}{dz^2} - 20i\beta\frac{dg}{dz}\frac{d^3g}{dz^3}\right)\\ &+ \frac{6\cdot 7}{g^8}\left(15i\beta\left(\frac{d^2g}{dz^2}\right)^2 + 5\frac{dg}{dz}\frac{d^4g}{dz^4} + 10\frac{d^2g}{dz^2}\frac{d^3g}{dz^3}\right)\\ &+ \frac{6\cdot 7\cdot 8}{g^9}\left(10\beta^2\left(\frac{dg}{dz}\right)^3 - 30i\beta\left(\frac{dg}{dz}\right)^2\frac{d^2g}{dz^2} - 10\left(\frac{dg}{dz}\right)^2\frac{d^3g}{dz^3} - 15\frac{dg}{dz}\left(\frac{d^2g}{dz^2}\right)^2\right)\\ &\left. + \frac{6\cdot 7\cdot 8\cdot 9}{g^{10}}\left(5i\beta\left(\frac{dg}{dz}\right)^4 + 10\left(\frac{dg}{dz}\right)^3\frac{d^2g}{dz^2}\right) - \frac{6\cdot 7\cdot 8\cdot 9\cdot 10}{g^{11}}\left(\frac{dg}{dz}\right)^5\right]e^{i\beta z}\end{aligned} \tag{21.5}$$

The fifth derivative is now evaluated at the pole z_o. According to Eq.(21) the values of g and its derivatives at the pole are

$$f = 1 - \frac{1}{a} \ln sech\, z$$

$$g_o = \left(\frac{df}{dz}\right)_o \tag{22}$$

$$\left(\frac{d^n g}{dz^n}\right)_o = \frac{1}{n+1}\left(\frac{d^{n+1} f}{dz^{n+1}}\right)_o$$

where the subscript o means that the quantities are evaluated at z_o. The values of g and its derivatives required are thus

$$g_o = \frac{1}{a} \tanh z_o = \frac{i}{a}(e^{2a}-1)^{1/2} \tag{23.1}$$

$$\left(\frac{dg}{dz}\right)_o = \frac{sech^2 z_o}{2a} = \frac{e^{2a}}{2a} \tag{23.2}$$

$$\left(\frac{d^2 g}{dz^2}\right)_o = -\frac{2}{3a} sech^2 z_o \tanh z_o = -\frac{2i}{3a} e^{2a}(e^{2a}-1)^{1/2} \tag{23.3}$$

$$\left(\frac{d^3 g}{dz^3}\right)_o = \frac{sech^2 z_o}{2a}(2\tanh^2 z_o - sech^2 z_o) = -\frac{e^{2a}}{2a}(3e^{2a}-2) \tag{23.4}$$

$$\left(\frac{d^4 g}{dz^4}\right)_o = -\frac{8}{5a}(sech^2 z_o \tanh^3 z_o - 2\, sech^4 z_o \tanh z_o) = \frac{8i}{5a} e^{2a}(3e^{2a}-1)(e^{2a}-1)^{1/2} \tag{23.5}$$

$$\left(\frac{d^5 g}{dz^5}\right)_o = \frac{8}{3a}\left(sech^2 z_o \tanh^4 z_o - \frac{11}{2} sech^4 z_o \tanh^2 z_o + sech^6 z_o\right) = \frac{4e^{2a}}{3a}(15e^{4a}-15e^{2a}+2) \tag{23.6}$$

For simplification, the following positive real factors of these derivatives are used

$$h_o = -i\, g_o = \frac{1}{a}(e^{2a}-1)^{1/2} \tag{24.1}$$

$$h_1 = \left(\frac{dg}{dz}\right)_o = \frac{e^{2a}}{2a} \tag{24.2}$$

$$h_2 = i\left(\frac{d^2g}{dz^2}\right)_o = \frac{2e^{2a}}{3a}(e^{2a}-1)^{1/2} \tag{24.3}$$

$$h_3 = -\left(\frac{d^3g}{dz^3}\right)_o = \frac{e^{2a}}{2a}(3e^{2a}-2) \tag{24.4}$$

$$h_4 = -i\left(\frac{d^4g}{dz^4}\right)_o = \frac{8e^{2a}}{5a}(3e^{2a}-1)(e^{2a}-1)^{1/2} \tag{24.5}$$

$$h_5 = \left(\frac{d^5g}{dz^5}\right)_o = \frac{4e^{2a}}{3a}(15e^{4a}-15e^{2a}+2) \tag{24.6}$$

In terms of these positive real quantities, the fifth derivative of G evaluated at the pole z_o is

$$\begin{aligned} i\left(\frac{d^5G}{dz^5}\right)_o = \frac{e^{-\beta y_o}}{h_o^6}\Bigg[&\beta^5+\frac{6}{h_o}(5\beta^4h_1-10\beta^3h_2+10\beta^2h_3-5\beta h_4+h_5) \\ &+\frac{6\cdot 7}{h_o^2}(10\beta^3h_1^2-30\beta^2h_1h_2+5\beta[4h_1h_3+3h_2^2]-5[h_1h_4+2h_2h_3]) \\ &+\frac{6\cdot 7\cdot 8}{h_o^3}(10\beta^2h_1^2-30\beta h_1^2h_2+5h_1[2h_1h_3+3h_2^2]) \\ &+\frac{6\cdot 7\cdot 8\cdot 9}{h_o^4}(5\beta h_1^4-10h_1^3h_2)+\frac{6\cdot 7\cdot 8\cdot 9\cdot 10}{h_o^5}h_1^5\Bigg] \end{aligned} \tag{25}$$

Then the Fourier transform is just the product of $2\pi\beta i$ and the residue at the pole

$$F = \frac{2\pi\beta}{5!}\, i\left(\frac{d^5G}{dz^5}\right)_o \qquad (26)$$

EXCITATION RATE COEFFICIENTS

With the transition probabilities P_{ab} calculated from Eq.(13.1), the rate coefficients can be determined. Just as done for vibrational transitions, the head on collisions are assumed to establish the functional form for the transition probability and the absolute magnitude of the rate coefficient is obtained by multiplying the result with a constant cross section S_o, which should be the order of 10^{-15} cm^2 for the ground state atoms. For the excited states this constant is increased by the range of the hydrogen like outer electron wave function

$$S_a = \frac{S_o}{(1-e_a/I)^2} \qquad (27)$$

where e_a is the electronic energy of state a and I is the ionization energy of the ground state of the atom. The rate coefficient is obtained by numerical integration over a Boltzmann distribution of collision energies

$$k_{ab} = \bar{u}\, S_o \int_{x_o}^{\infty} (S_a/S_o)\; P_{ab}\; x\; e^{-x}\, dx \qquad (28)$$

where $\bar{u}$ is the mean molecular velocity in center of mass coordinates, x is the dimensionless collision energy in units of kT, and x_o is the activation energy in these units. S_a/S_o and P_{ab} are calculated as functions of the dimensionless collision energy and the integral is performed numerically by quadrature.

EXAMPLE RESULT FOR AN N-N COLLISION

The relations developed above are now used to calculate the probability of transition of an N atom in the ($3s^2P$) state to the ($4s^2P$) state when it is perturbed by a collision with an N atom in the ($^4S°$) ground state, which is taken to be unchanged in the collision.

The polarizability of the ground state atom is given by Eq.(15). The $^4S°$ state has two strong absorption lines at 83336 cm^{-1}

and at 88135 cm^{-1} with f numbers of .35 and .13 respectively[14]. These lines are so far from the transition frequency ω_{ab}

$$\omega_{ab} = \omega_b - \omega_a = 104200 - 86200 = 18000 cm^{-1} \qquad (29.1)$$

that the damping factor can be neglected. Then

$$\frac{\alpha}{a_o^3} \approx \frac{e^2}{4\pi^2 a_o^3 mc^2} \sum_i \frac{f_i}{\omega_i^2 - \omega_{ab}^2} = 3.386 \qquad (29.2)$$

and the dimensionless factor required in Eq.(13.1) is

$$(\alpha/a_o^3)^2 \left(\frac{e^2/a_o}{\hbar\omega_{ab}}\right)^2 = 1689 \qquad (29.3)$$

The matrix element H_{ab} is expected to be the order of 10. This factor is approximated using Slater type screened wave functions

$$R_a = R_{300} = \frac{2Z_3^{3/2}}{9\sqrt{3}} (3 - 2Z_3 r + \frac{2}{9} Z_3^2 r^2) e^{-Z_3 r/3} \qquad (30.1)$$

$$R_b = R_{400} = \frac{Z_4^{3/2}}{32} (8 - 6Z_4 r + Z_4^2 r^2 - Z_4^3 r^3/24) e^{-Z_4 r/4} \qquad (30.2)$$

The effective nuclear charges are adjusted to agree with the observed energy levels

$$Z^2 = n^2 (I - E) / (e^2/2a_o)$$

$$Z_a = [9(117345 - 86200)/109571]^{1/2} = 1.605 \qquad (31)$$

$$Z_b = [16(117345 - 104200)/109571]^{1/2} = 1.385$$

To the accuracy of this approximation the transition matrix element is

$$H_{ab} = \int_o^{\pi} \cos^2\theta \sin\theta \, d\theta \int_o^{\infty} (R_b r^2 R_a) \, r^2 dr \qquad (32.1)$$

$$H_{ab} = \frac{1}{3}\frac{(Z_a Z_b)^{3/2}}{144\sqrt{3}}\int_o^\infty \Big|24-(16Z_a+18Z_b)\,r+\Big(\frac{16}{9}Z_a^2+12Z_aZ_b+3Z_b^2\Big)\,r^2 \qquad (32.2)$$
$$-\Big(\frac{4}{3}Z_a^2Z_b+2Z_aZ_b^2+\frac{Z_b^3}{8}\Big)\,r^3+\Big(\frac{2}{9}Z_a^2Z_b^2+\frac{Z_aZ_b^3}{12}\Big)\,r^4-\frac{Z_a^2Z_b^3}{9\cdot 12}r^5\Big|e^{-Zr}dr$$

where

$$Z = \frac{Z_a}{3}+\frac{Z_b}{4} = .881 \qquad (32.3)$$

Thus

$$H_{ab}^2 = (-8.123)^2 = 65.98 \qquad (33)$$

Finally the transition probability is a function of collision energy, which for this particular transition is given by

$$P_{ab} = 1.113\cdot 10^5\,\frac{F_{ab}^2}{(R_o/a_o)^{12}} \qquad (34)$$

To evaluate the Fourier transform of Eq.(13.3) the constants of the repulsive potential of Eq.(9) must be specified. For the purely repulsive potential that occurs most frequently between colliding atoms, the constants A = 305 ev and L = .35 Å have been chosen. These constants fit the potential given by Gilmore[16] fairly well; they are assumed to also approximate the repulsion with the excited atom except that the size of the cross section is increased as in Eq.(27). The transition probability of Eq.(34) calculated for this potential interaction is shown on Fig.(4) as a function of collision energy. Except at collision energies the order of 30 ev or larger these probabilities are small compared with unity so that the small perturbation method is justified at low temperatures. However, at high temperatures the tail of the Boltzmann distribution contributes much to the rate coefficient where the small perturbation method breaks down. To compensate for this the transition probabilities are limited to unity at collision energies above 30 ev.

The rate coefficient is obtained by integrating the transition probability over a Boltzmann distribution of collision energies for a range of different temperatures. Fig.(5) shows k_{ab} as a function of temperature between 5000 and 50000°K. These rate coefficients are considerably smaller than the free electron excitation rates as expected. The relation for electron collision excitation of the

same transition, that is the excitation of $N(3s^2P)$ to $N(4s^2P)$, is shown by the dashed line on Fig.(5); Park's expression[6] for this rate coefficient is

$$k_{5\text{-}8} = 4.3 \cdot 10^{16} \left(\frac{10000}{T_e} \right)^{.14} e^{-25422/T_e} \quad cc/mol\text{-}sec \qquad (35)$$

The rate coefficients calculated for ground state N atom collision excitation of this transition are given as a function of temperature in the following table.

TABLE I. RATE COEFFICIENT FOR $N(3s^2P) + N(^4S^o) \rightarrow N(4s^2P) + N(^4S^o)$

T,degK	k,cc/mol-sec	$\log_{10}k$
5000	1.960×10^{-2}	-1.708
10000	1.066×10^{5}	5.028
15000	1.708×10^{8}	8.232
20000	1.472×10^{10}	10.168
25000	2.688×10^{11}	11.430
30000	1.940×10^{12}	12.288
35000	7.897×10^{12}	12.898
40000	2.354×10^{13}	13.372
45000	5.544×10^{13}	13.744
50000	1.096×10^{14}	14.040

This sample calculation illustrates how other transition reaction rates could be determined by this method. Although the transition matrix elements are not highly accurate, these are not the crucial factors that the Fourier transforms are as far as establishing the correct magnitude of the transition probabilities. Once the rate coefficients have been determined for all the important transitions, the relaxation rates can be found from Eq.(7) using the Master Equation from Eq.(5) to obtain the rate of change in electronic state energy caused by atom-atom collisions.

CONCLUDING REMARKS

The relaxation times for electronic excitation due to electron bombardment of atoms has been found to be quite short, so that electron kinetic temperature T_e and the electron excitation temperature T^* should equilibrate quickly whenever electrons are present. However, once equilibration has been achieved, further energy to the excited electronic states and to the kinetic energy of free electrons must be fed in by collisions with heavy particles that cause vibrational and electronic state transitions.

The rate coefficients for excitation of electronic states produced by heavy particle collision have not been well known. However, a relatively simple semi-classical theory has been developed here which is analytic up to the final integration over a Boltzmann distribution of collision energies; this integral can then be evaluated numerically by quadrature. Once the rate coefficients have been determined, the relaxation of electronic excitation energy can be evaluated and compared with the relaxation rates of vibrational excitation. Then the relative importance of these two factors, electronic excitation and vibrational excitation by heavy particle collision, on the transfer of energy to free electron motion, can be assessed.

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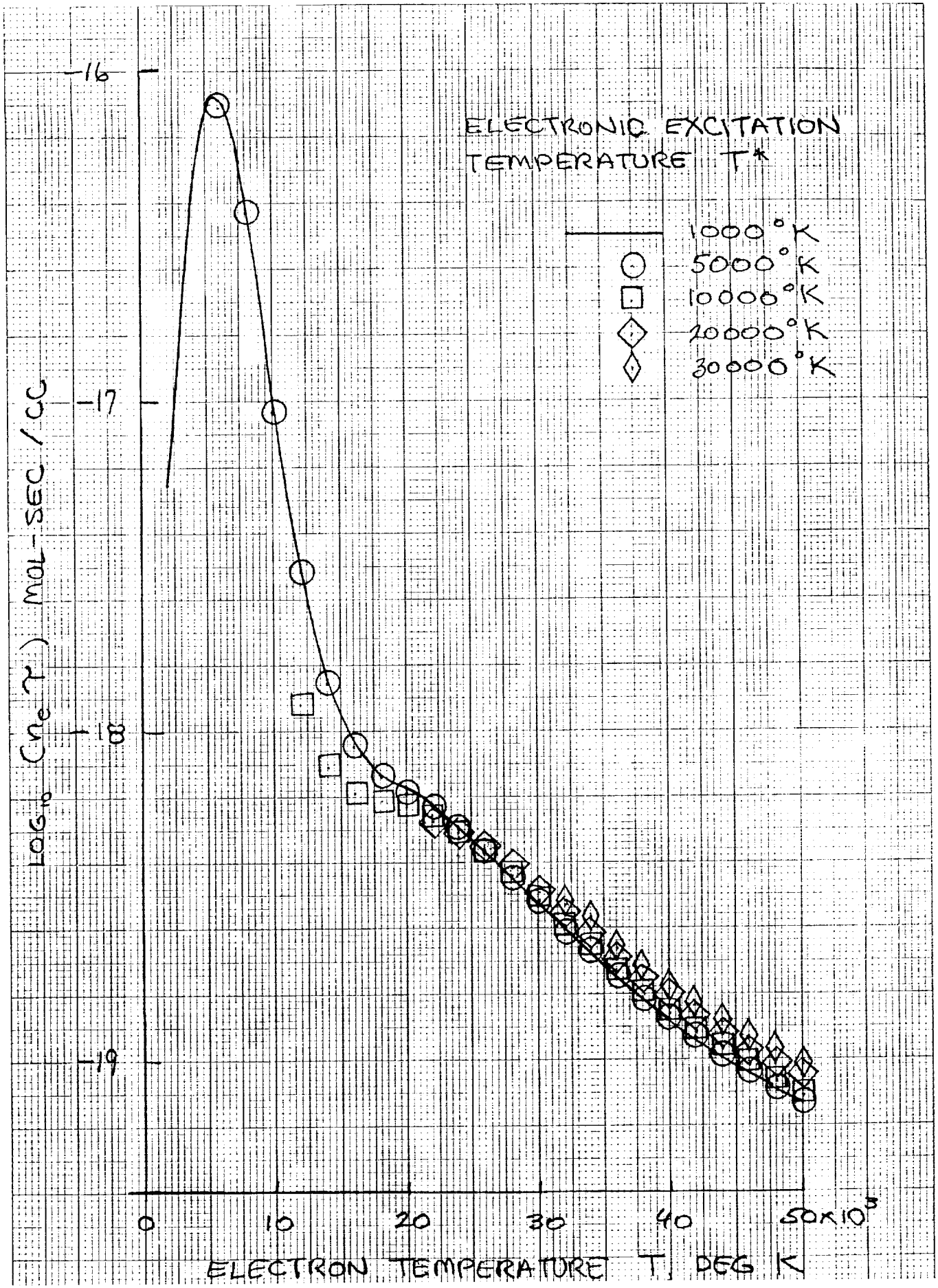
FIG.(1) RELAXATION OF N ATOM ELECTRONIC ENERGY BY ELECTRON IMPACT

FIG.(2) RELAXATION OF O ATOM ELECTRONIC ENERGY BY ELECTRON IMPACT

FIG.(3) EXPONENTIAL COLLISION POTENTIAL PLUS INDUCED DIPOLE INTERACTION

FIG.(4) PROBABILITY OF ATOMIC N($3s^2P$) TRANSITION TO ATOMIC N($4s^2P$) DUE TO COLLISION WITH ATOMIC N($^4S^o$) AS A FUNCTION OF COLLISION ENERGY

FIG.(5) RATE COEFFICIENTS AS A FUNCTION OF TEMPERATURE FOR ATOMIC N($3s^2p$) TRANSITION TO ATOMIC N($4s^2P$) DUE TO COLLISIONS WITH ELECTRONS AND ($^4S^o$)N ATOMS



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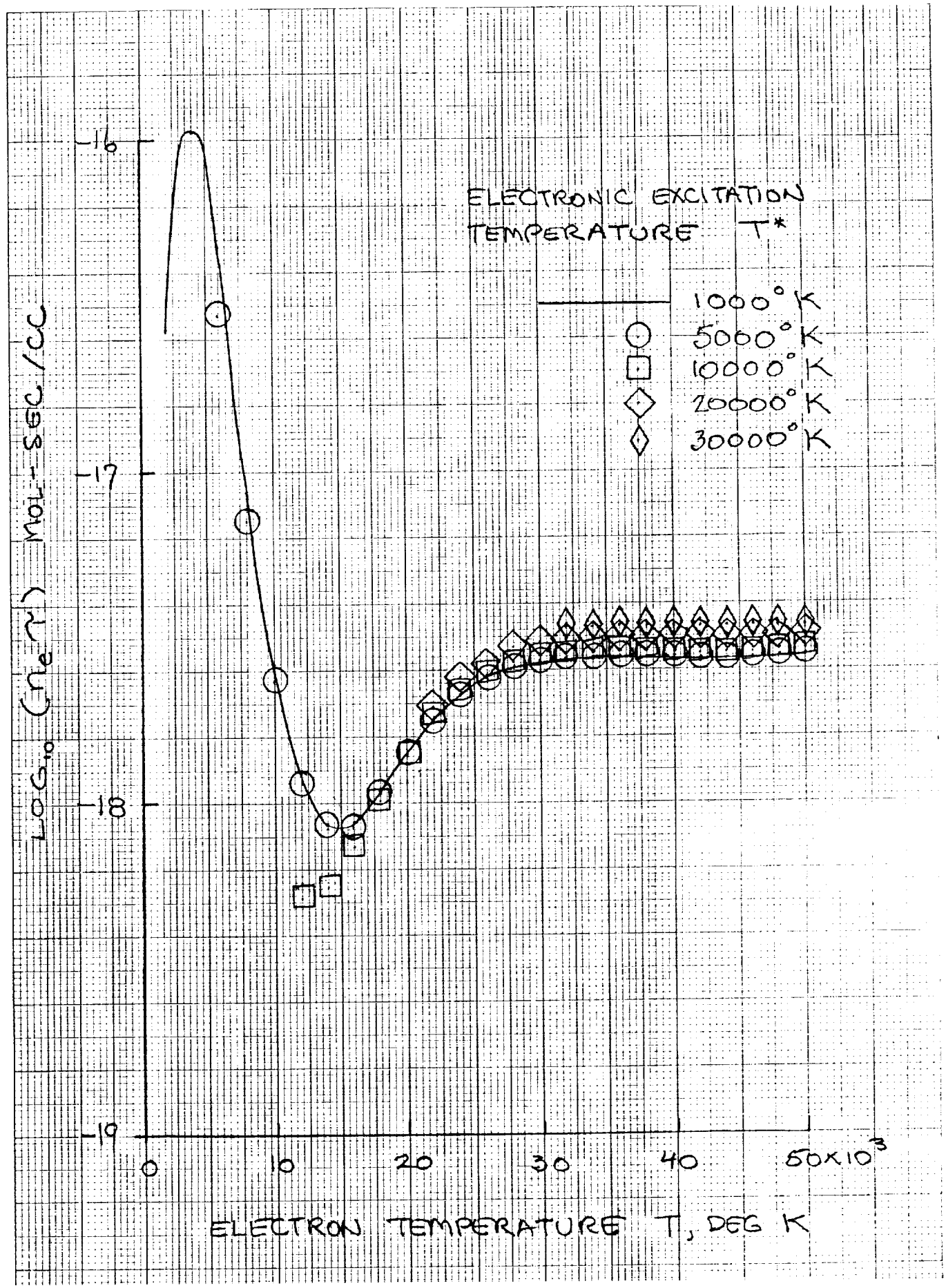
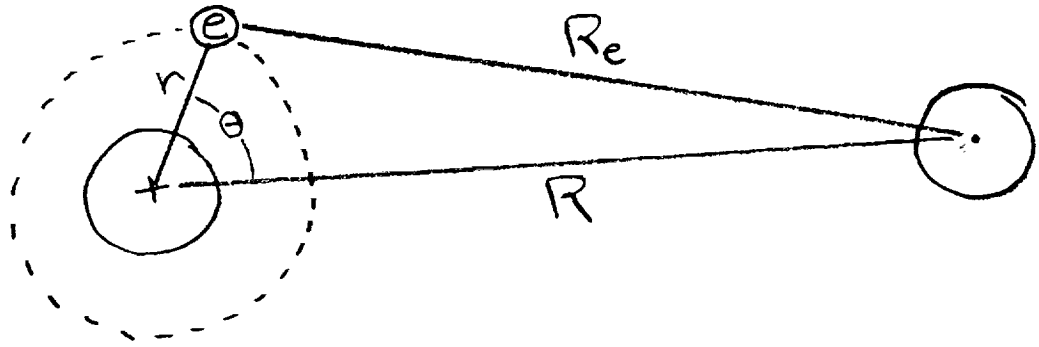


FIG.(2) RELAXATION OF O ATOM ELECTRONIC ENERGY BY ELECTRON IMPACT



ELECTRIC FIELD PRODUCED BY EXCITED ELECTRON-ION DIPOLE AT THE POSITION OF AN APPROACHING NEUTRAL COLLISION PARTNER

$$E = -\frac{e}{R_e^2} + \frac{e}{R^2}$$

$$\simeq -\frac{e}{R^2}\left(1 + \frac{2r}{R}\cos\theta \cdots - 1\right)$$

$$\simeq -\frac{2er\cos\theta}{R^3}$$

TOTAL INTERACTION ENERGY FOR EXPONENTIAL REPULSION AND POLARIZATION INTERACTION

$$U = A e^{-R/L} - \frac{4\alpha e^2 r^2 \cos^2\theta}{R^6}$$

FIG.(3) EXPONENTIAL COLLISION POTENTIAL PLUS INDUCED DIPOLE INTERACTION

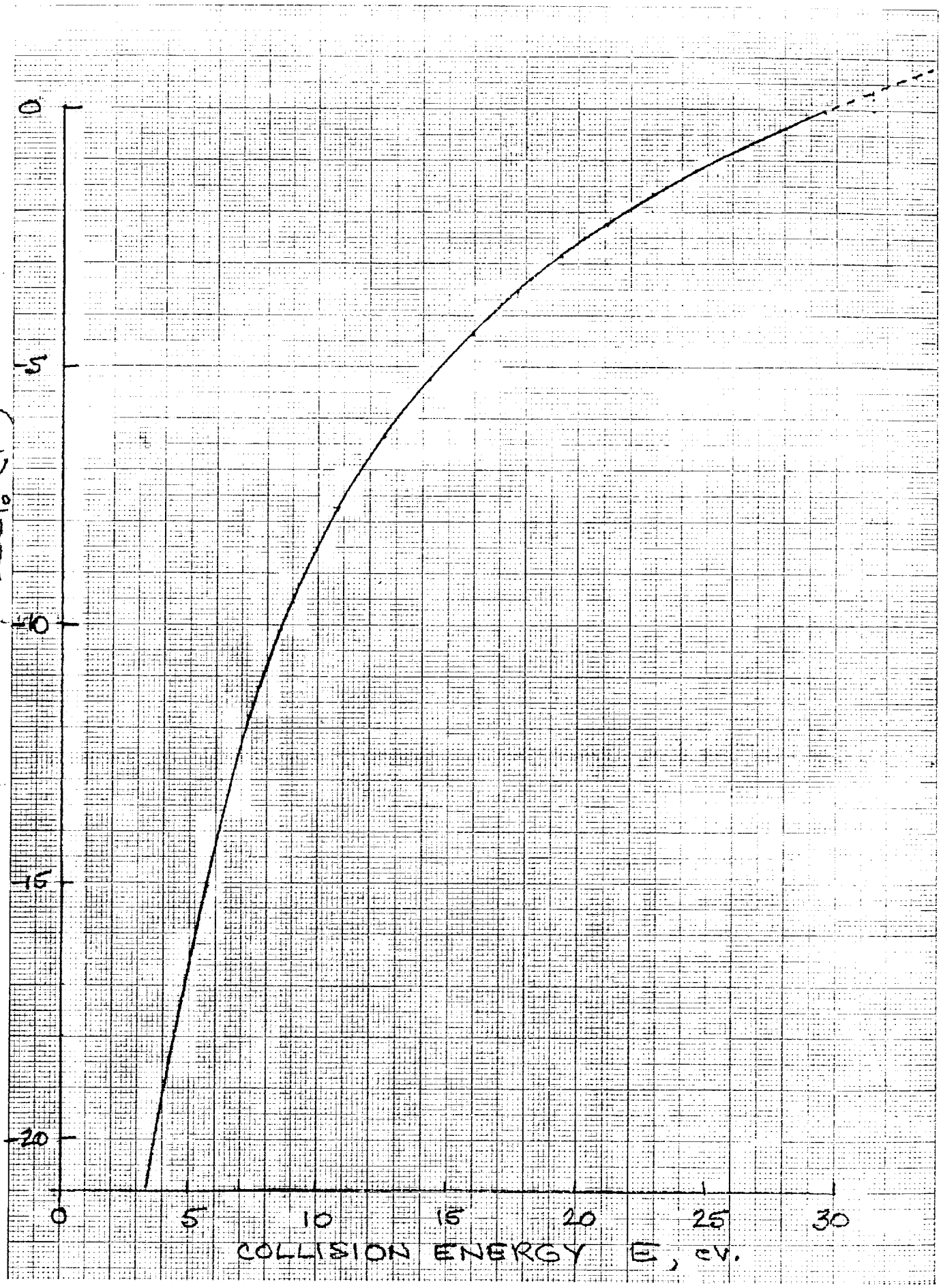
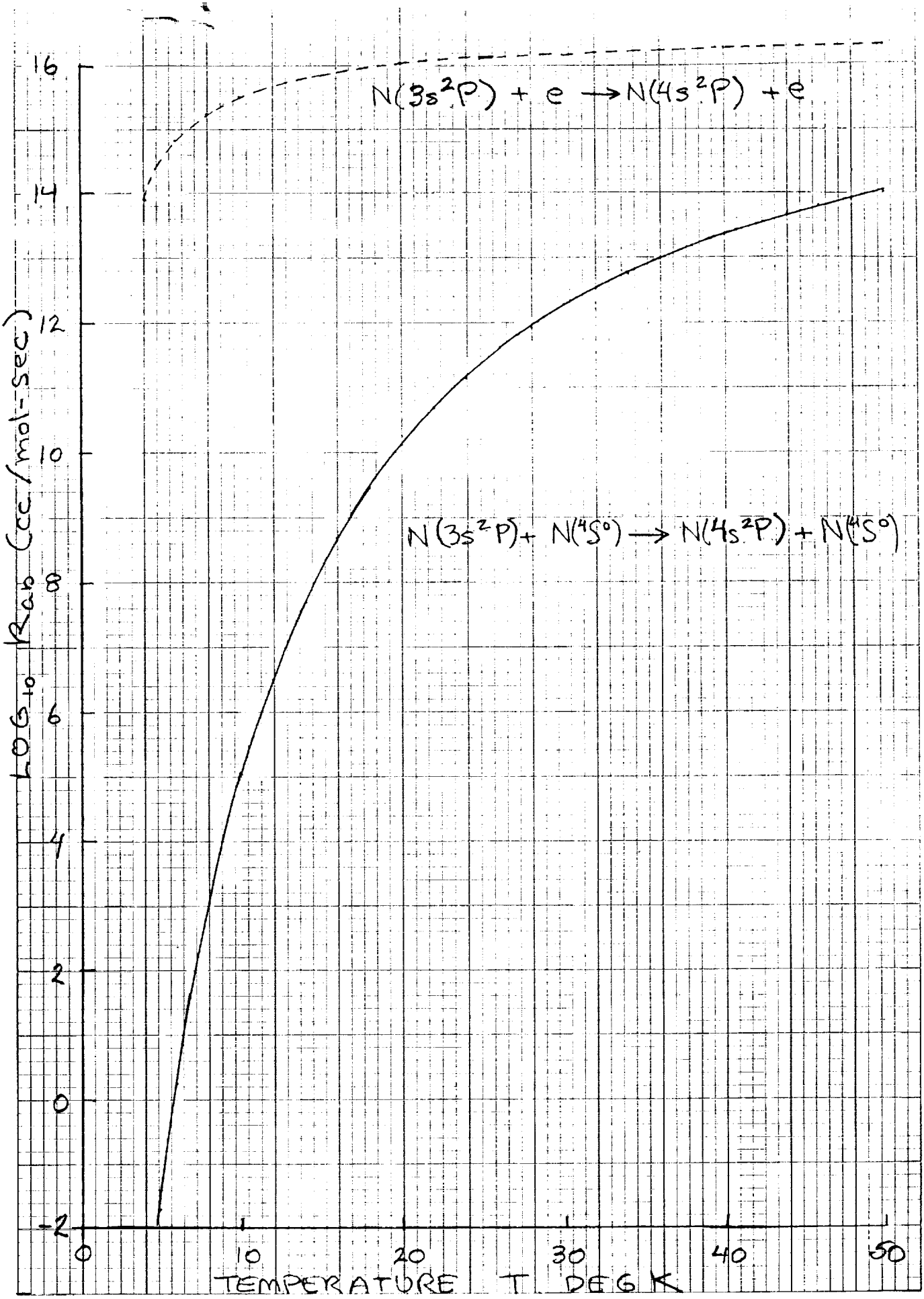


FIG.(4) PROBABILITY OF ATOMIC N($3s^2P$) TRANSITION TO ATOMIC N($4s^2P$) DUE TO COLLISION WITH ATOMIC N($^4S°$) AS A FUNCTION OF COLLISION ENERGY



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